| (51) International patent classification[7]: C07C 2/08 | A1 | (11) International Publication Number: WO 00/69795 |
| | | (43) International Publication Date: November 23, 2000 (11/23/00) |

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| (21)  International file number: PCT/EP00/04286 (22)  International application date:   May 11, 2000 (05/11/00) (30)  Priority dates: 199 22 038.7    May 12, 1999 (05/12/99) DE (71)  Applicant (for all target states except the US): BASF AKTIENGESELLSCHAFT (DE/DE); D-67056 Ludwigshafen (DE) (72)  Inventors, and (75)  Inventors/Applicants (only for the US): SCHULZ, Ralf [DE/DE]; Maulbronner Hof 35, D-67346 Speyer (DE). WALTER, Marc [FR/DE]; Hans-Holbein-Strasse 5d, D-67227 Frankenthal (DE). NEUMANN, Hans-Peter [DE/DE]; Mittelstrasse 12, D-67067 Ludwigshafen (DE). BROX, Wolfgang [DE/DE]; Im Grund 13, D-69118 Heidelberg (DE). (74)  Attorneys: KINZEBACH, Werner etc., Ludwigsplatz 4, D-67059 Ludwigshafen (DE) | (81)  Target states: CN, JP, KR, SG, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Disclosed With international search report |

(54)    Title:    A METHOD FOR THE OLIGOMERIZATION OF $C_2$-$C_8$-OLEFINS

(57)    Abstract

A method for the oligomerization of $C_2$-$C_8$-olefins, in which a flow of an olefin-containing hydrocarbon mixture is guided successively through "n" adiabatically operated reaction zones on a heterogeneous catalyst that contains nickel, where $n \geq 2$, in which case the hydrocarbon mixture experiences a temperature increase $\Delta T_{react}$ in each reaction zone and the hydrocarbon mixture enters the first reaction zone at a temperature of $T_{enter}$ and is prior to entering the next reaction zone cooled to a temperature that is higher or lower than $T_{enter}$ by up to 20 °C, and in which case the respective catalyst volumes of the individual reaction zones are sized such that the $\Delta T_{react}$ difference does not exceed 20 °C.

A method for the oligomerization of $C_2$-$C_8$-olefins

## Description

This invention concerns a method for the oligomerization of $C_2$-$C_8$-olefins in several successive reaction zones.

Olefins with between 2 and 8 carbon atoms or their mixtures are available from FCC-units (Fluidized Catalyst Cracking) and also from steam crackers in large quantities. It is known to use the respective $C_4$-section, i.e., a mixture that basically consists of butenes and butanes, for the production of oligomers and particularly of octenes and dodecenes, possibly after the iso-butene has been separated. After a hydroformylation and subsequent hydration to form the respective alcohols, octenes as well as dodecenes are used for the production of softening agents or tensides.

The large-scale oligomerization is run under a homogeneous or heterogeneous catalysis. The homogeneously catalyzed method exhibits the disadvantage that the catalyst must be separated from the reaction mixture. This separation phase forms waste flows that must be processed in an expensive manner. Furthermore, it is impossible to regenerate the homogeneous catalyst.

The above-described disadvantages do not exist for the heterogeneously catalyzed olefin oligomerization. The most important heterogeneously catalyzed olefin oligomerization methods used by the industry are listed, for example, in A. Chauvel and G. Lefebvre, Petrochemical Process, Edition Technip (1989), page 183-187 and in F. Asinger, The Petrochemical Industry, Akademie-Verlag (1971), page 278-299.

The oligomerization reaction on a heterogeneous catalysts proceeds in an exothermal manner. Because of lower investment cost, one strives to run the olefin oligomerization in adiabatically operated reactors. In contrast to the isothermal reaction, in which the reaction heat that develops in an exothermal reaction is removed with cooling or temperature control devices and the temperature is thus maintained at a constant level, i.e., isothermal, the adiabatic reaction is defined as an operation, in which the heat released by an exothermal reaction is almost exclusively absorbed by the reaction mixture in the reactor and there is no cooling with cooling devices. In the adiabatic operation, the removal of the formed reaction products as well as of the reaction heat is achieved with the reaction mixture flow guided through the reaction zones. Accordingly, the temperature of the reaction mixture flow increases along the reactor with a progressing reaction process. The temperature difference between outlet and inlet temperature of the reaction mixture is sometimes called temperature density.

Regulating the inlet temperature of the hydrocarbon mixture represents one possibility to control the process. To save energy cost, one prefers an inlet temperature for the hydrocarbon mixture that is as close as possible to the ambient temperature. However, the inlet temperature must be high enough to ensure the desired catalyst activity level and reaction velocity and thus the targeted yield. Furthermore, it is necessary to consider the fact that the catalyst activity decreases with an increasing catalyst service. To reach a higher reaction velocity and to thus compensate for the catalyst activity level that decreases over time, the inlet temperature is generally increased for a

decreasing catalyst activity. However, the inlet temperature cannot be increased to just any level. The maximum temperature that can be reached by the hydrocarbon mixture when passing through the reaction zone is restricted by safety aspects and practical considerations such as the maximum pressure for which the plant was designed. When the catalyst activity has decreased to such an extent that the hydrocarbon mixture has reached this maximum temperature when leaving the reaction zone, the catalyst is exhausted and must be replaced with a new catalyst. Accordingly, the maximum inlet temperature is determined by the maximum allowed reactor outlet temperature less the temperature density occurring through the reactor.

The older application DE-197 505 31.7 describes a method for the production of octenes and dodecenes with the oligomerization of hydrocarbon flows that contain butene-1 and/or butene-2 and butane across a heterogeneous catalyst that contains nickel, in which case one returns such quantities of butane that have been separated from the reaction mixture and unreacted butene to the oligomerization reaction that the maximum oligomer concentration in the reaction mixture does not exceed 25% by weight in relation to the total reaction hydrocarbon mixture.

A proposal to divide an adiabatically operated solid bed reactor into several reaction zones has already been made, in which case the reaction mixture is cooled between the individual reaction zones through an indirect heat exchange or by mixing-in cold gas; see, for example, M. Baerns (Publisher) Chem. Reaction Technology, Thieme-Verlag, 1987, page 249.

The older application DE 199 15 357.4 describes a method for the oligomerization of $C_2$-$C_8$-olefins on a heterogeneous catalyst that contains nickel, in which case the catalyst is pretreated with the hydrocarbon mixture prior to the contact, i.e., it is brought into contact with a hydrocarbon mixture that contains less olefins. It is indicated that the operating phase can be executed in a reactor cascade consisting of two or more oligomerization reactors, in which case the partially reacted reaction mixture is cooled after leaving one reactor and prior to entering the next cascade reactor.

The document US 4,942,021 yields a continuous multi-stage method for the processing of a feed that contains a low olefin, in which case the feed is guided across an acid zeolite catalyst in a first reactor; the discharge from the first reactor is cooled by injecting water; the mixture consisting of reactor discharge and water is guided across a metal-containing zeolite catalyst in a second reactor.

The document US 5,019,357 discloses a two-stage catalytic system to convert a low olefin feed to heavier liquid hydrocarbons.

The temperature density occurring in the individual reaction zones is lower than that in a uniform reactor with the same catalyst volume. Accordingly, the temperature range available to vary the inlet temperature to compensate for the declining catalyst activity is larger for this arrangement. The catalyst can thus be used for a longer period and this represents a cost advantage.

It was determined that the temperature density in the first reaction zone is substantially higher than in the second reaction zone, when oligomerization catalysts that contain nickel are used at a uniform catalyst volume distribution across two reaction zones, for example. The temperature range, across which the inlet temperature can be varied, is restricted by the higher temperature

density in the first reaction zone, since the maximum temperature the hydrocarbon mixture is permitted to reach occurs sooner in the first than in the second reaction zone. Accordingly, it is impossible to take full advantage of the upper temperature limit in the second reaction zone; the catalyst of the second reaction zone is still active, while the catalyst in the first reaction zone must be replaced already. The catalyst activity level cannot be fully exhausted in the second reaction zone.

Accordingly, the task of this invention consists in presenting a method that permits the best-possible full use of the catalyst activity.

It was found that this task can be solved by distributing the catalyst volume to the reaction zones in such a manner that the temperature densities occurring in the individual reaction zones are as equal as possible.

Accordingly, the object of the invention consists of a method, in which a flow of an olefin-containing hydrocarbon mixture is guided successively through "n" adiabatically operated reaction zones on a heterogeneous catalyst that contains nickel, where $n \geq 2$, in which case the hydrocarbon mixture experiences a temperature increase $\Delta T_{react.}$ in each reaction zone and the hydrocarbon mixture enters the first reaction zone at a temperature of $T_{enter}$ and is prior to entering the next reaction zone cooled to a temperature that is higher or lower than $T_{enter}$ by up to 20 °C, characterized by the fact that the relative catalyst volumes of the individual reaction zones are sized such that the $\Delta T_{react.}$ difference does not exceed 20 °C.

Accordingly, the relative catalyst volumes of the individual reaction zones are sized such that the following equation applies to all i,j-pairs

$$\Delta T_{react.}^{i} - \Delta T_{rect.}^{j} \leq 20 \text{ °C},$$

where $\Delta T_{react.}^{i}$ and $\Delta T_{rect.}^{j}$ represent the temperature increase experienced by the hydrocarbon mixtures in reaction i or j, n is $\leq 2$, i varies between 2 and n and j between 1 and i-1.

$\Delta T_{react.}^{i} - \Delta T_{rect.}^{j} \leq 10$ °C is preferred and $\leq 5$ °C is particularly preferred. In other words, the respective catalyst volumes shall be sized such that the heat density values occurring in the individual reaction zone range within a temperature band of 20 °C, preferably of 10 °C and particularly preferred of 5 °C. The number "n" for the reaction zones preferably varies between 2 and 5 and particularly between to 2 and 3.

To meet the above-mentioned condition, the catalyst volume of the second and of each further reaction zone - if present - is larger than that of the previous reaction zone, i.e., generally by between approximately 30 and 60% by volume. In the preferred case of two reaction zones (n=2), the ratio between the catalyst volume of the first reaction zone and the catalyst volume of the second reaction zone preferably varies between 30:70 and 45:55 and the ratio is particularly 40:60. When using reaction zones with basically uniform cross-sections, the second and each next reaction zone is thus longer than the previous reaction zone.

The hydrocarbon mixture enters the first reaction zone at a temperature of $T_{enter}$. Due to the

exothermal reaction in the reaction zone, the mixture leaves this zone at a higher temperature. Prior to entering a further reaction zone, it is cooled to a temperature of within 20 °C, preferably of within 10 °C and particularly preferred of within 5 °C of $T_{enter}$. The cooling of the hydrocarbon mixture is preferably achieved with an indirect heat exchange, generally with suitable heat exchangers or similar. It is advantageous to use heat exchangers that are arranged in series and can be turned-on or turned-off when required. An injecting of cooling agents or of a fresh olefin-containing feed in the partially reacted hydrocarbon mixture is not preferred. It is also preferred that the composition of the partially reacted hydrocarbon mixture remains unchanged between the reaction zones, i.e., it is preferred that no components are separated or mixed-in.

To compensate for the decrease in the catalyst activity level over time, $T_{enter}$ must be selected higher as a function of the period the catalyst has been in service. Particularly when using a hydrocarbon mixture that contains $C_4$-olefins, $T_{enter}$ may be selected between 20 and 120 °C. The maximum outlet temperature is essentially determined by safety aspects and - in specific preferred examples of the invention, in which one works with liquid mixtures - by the fact that the hydrocarbon mixture still is in the liquid phase at the selected pressure.

The reaction zones for the method in accordance with the invention are operated adiabatically. An adiabatic reaction refers to an operation, in which the heat created during the oligomerization at the heterogeneous catalyst is practically in a complete manner removed by the mixture and there is no cooling with cooling or temperature control devices. It is also understood that a negligibly small part of the heat released during the exothermal reaction is also and unavoidably absorbed by the reactor body and is transferred to the environment through heat conduction and heat dissipation. From a technical point of view, an adiabatic reaction thus refers to an operation, in which the whole reaction heat is absorbed by the reaction mixture and is removed with it from the reactor, i.e., with the exception of the reaction heat segment that is transferred from the reactor to the environment by way of a natural heat conduction and dissipation.

The usable and heterogeneous catalysts that contain nickel may exhibit different structures. One basically takes into consideration known catalysts such as those described in C.T. O'Connor et al., Catalysis Today, Vol. 6 (1990), page 336-338. Nickel catalysts bonded to carriers are used in particular. The carrier materials may consist of silicic acid, oxide of aluminum, alumino silicates, alumino silicates with layer structures and of zeolites such as mordenite, faujasite, zeolite X, zeolite Y and ZSM-5, zirconium oxide treated with acids or sulfated titanium dioxide. Particularly suited are precipitation catalysts that are obtainable by mixing aqueous solutions of nickel salts and silicates such as sodium silicate with nickel nitrate and possibly aluminum salts such as aluminum nitrate, followed by a calcining. One can also use catalysts that are obtained by incorporating $Ni^{2+}$-ions by way of an ion exchange in natural and/or synthetic layer silicates such as montmorillonite. Suitable catalysts can also be obtained by impregnating acidic acid, oxide of aluminum or alumo silicates with aqueous solutions of soluble nickel salts such as nickel nitrate, nickel sulfate or nickel chloride, followed by a calcination.

Preference is given to catalysts that contain nickel oxide.
Particularly preferred are catalysts that basically consist of NiO, $SiO_2$, $TiO_2$ and/or $ZrO_2$ as well as possibly of $Al_2O_3$. Such catalysts are particularly preferred when the method in accordance with the invention is used for the oligomerization of butene. They lead to a preference for a dimerization

with respect to the formation of higher oligomers and they mostly deliver linear products. Mostly preferred is a catalyst whose active components consist of between 10 and 70% by weight nickel oxide, between 5 and 30% by weight titanium dioxide and/or zircon dioxide, between 0 and 20% by weight aluminum oxide and the rest of silicon oxide. Such a catalyst can be obtained with a precipitation of the catalyst mass at a pH-value of between 5 and 9 by adding an aqueous solution containing nickel nitrate to an alkali water glass solution that contains titanium dioxide and/or zirconium dioxide, followed by a filtering, drying and tempering at between 350 and 650 °C. Reference is made here to DE-43 39 713 for details regarding the production of these catalysts. Reference is also made to the full content of the disclosure in this document and the prior art cited therein.

The catalyst is preferably available in solid pieces such as in the form of pellets with a diameter of between 2 and 6 mm and a height of between 3 and 5 mm, in the form of rings with an outside diameter of between 5 and 7 mm, a height of between 2 and 5 mm and a hole diameter of between 2 and 3 mm, or in the form of strands of different lengths and with a diameter of between 1.5 and 5 mm. Such forms are obtained in a generally known manner by pellet-compression or extrusion and in most cases with the help of a pellet-compressing agent such as graphite or stearic acid.

Although preference is given to using the same catalyst in all reaction zones, it is possible to use different oligomerization catalysts in the individual reaction zones.

Although it is also possible to use pure olefin flows, the olefin-containing hydrocarbon mixture used here consists of a mixture that essentially contains olefins and saturated hydrocarbons. A preferred mixture contains between 50 and 100% and particularly between 60 and 100% by weight $C_2$-$C_8$-olefins and preferably $C_4$-$C_6$-Olefins, particularly butene. When using $C_4$-hydrocarbon mixtures, one successfully uses those with an olefin content of between 50 and 95% by weight and particularly of between 60 and 90% by weight. The olefin fraction may consist of a single olefin such as n-hexene, propylene or mixture of isomeric olefins such as isomeric butene, or a mixture of olefins with different carbon atom numbers such as mixtures of 3-hexene and 2-pentene, propylene and butene or propylene and ethene. The saturated hydrocarbons contained in the mixture generally have the same carbon atom number than the olefin fraction. In view of the properties exhibited by the oligomerization products, it is often preferred that the hydrocarbon mixture to be used contains less than 5% by weight and particularly less than 3% by weight of branched olefins in relation to the olefin fraction.

A preferred mixture contains between 50 and 95% by weight and preferably between 60 and 90% by weight butene and between 5 and 50% by weight and preferably between 10 and 40% by weight butane. The butene fraction preferably includes less than 5% and particularly preferred less than 3% by weight iso-butene (in relation to the butene fraction). The butene fraction generally has the following composition (in relation to the butene fraction):

| | |
|---|---|
| 1-butene: | 1 to 99% by weight |
| cis-2-butene: | 1 to 75% by weight |
| trans-2-butene: | 1 to 75% by weight |
| iso-butene: | 1 to 5% by weight |

A particularly preferred application material is formed by the so-called Raffinate II that consists of

an iso-butene-depleted $C_4$-section from a FCC-unit or a steam cracker. Raffinate II may have the following typical composition:

| | |
|---|---|
| i- and n-butane: | 30% by weight |
| i-butene: | 2% by weight |
| 1-butene: | 35% by weight |
| trans-2-butene: | 19% by weight |
| cis-2-butene: | 14% by weight |

Hydrocarbon mixtures that are available on a large scale and can be considered as mixtures to be used for the presented invention often contain compounds that act as catalyst poisons and deactivate the oligomerization catalyst. This includes oxygen-containing compounds such as alcohols, aldehydes, ketones and ethers as well as nitrogen-containing, sulfur-containing and halogen-containing compounds. The presence of such catalyst poisons would lead to an undesirable decrease in the catalyst activity level.

For that reason and according to a preferred aspect of the invention, the hydrocarbon mixture is guided across an adsorption agent to remove catalyst poisons prior to bringing the mixture into contact with the catalyst. Suitable adsorption agents consist of molecular sieves, preferably those with a pore diameter of more than 4 Å to 15 Å. Molecular sieves may consist of crystalline, natural aluminum silicates such as layer lattice silicates as well as synthetic molecular sieves. Also suited are commercially available molecular sieves such as the types manufactured by the companies Bayer AG, Dow, Union Carbide, Laporte or Mobil. These molecular sieves may be zeolite of the types A, X and Y. Also suitable are synthetic molecular sieves that in addition to silicon and aluminum as main components contain other atoms as secondary components. These may be incorporated in the zeolites by way of an ion exchange with exchangeable cations. An exchange with rare earths such as gallium, indium or lanthanum, or with nickel, cobalt, copper, zinc or silver shall be listed here as examples. Furthermore, it is also possible to use synthetic zeolites, in which other atoms such as boron or phosphorous have been incorporated in the lattice through a co-precipitation.

Further suitable adsorption agents consist of aluminum oxide, aluminum phosphate, silicon dioxide, siliceous earth, titanium dioxide, zircon dioxide, polymeric adsorption agents and mixtures thereof. The guiding of the olefin-poor hydrocarbon mixture across the adsorption agent is appropriately achieved on a solid bed or moving bed. The hydrocarbon mixture may be in the gaseous or liquid state when passing across the adsorption agent; the liquid phase is preferred, however.

The concentration of compounds that contain oxygen, sulfur, nitrogen, and halogen in the hydrogen mixture preferably amounts to less than 1 ppm by weight and particularly to less than 0.5 ppm by weight.

When diolefins or alkines are present in the hydrocarbon mixture, they are removed from the mixture to less than 10 ppm by weight, particularly to less than 5 ppm by weight and particularly preferred to less than 1 ppm by weight prior to the oligomerization. Diolefins and alkines are removed through a selective hydration according to EP-81041 and DE-15 68 542.
The oligomerization reaction preferably occurs at temperatures of between 30 and 280 °C, particularly of between 30 and 140 °C and particularly preferred of between 40 and 130 °C, and at

a pressure of between 10 and 300 bar, preferably of between 15 and 100 bar and particularly of between 20 and 70 bar. In that regard, the pressure is selected appropriately in such a manner that the hydrocarbon mixture is in the liquid phase at the set temperature.

The reaction zones generally consist of cylindrical reactors that contain the catalyst, through which the preferably liquid reaction mixture flows from the top to the bottom or vice-versa. The reaction zones may also consist of sections in a uniform reactor housing.

After leaving the last reaction zone, the formed oligomers are in a generally known manner separated from the unreacted olefins and saturated hydrocarbons. The separated oligomers can be purified in a subsequent fractionation phase.

In a preferred example of the invention, the maximum oligomer concentration in the reaction mixture is limited to 30% by weight, preferably to 25% by weight and particularly to 22% by weight in relation to the reaction hydrocarbon mixture. The concentration generally does not fall below a lower limit of 10% by weight oligomers in the reacted reaction mixture prior to its processing. With this measure, it is possible to substantially increase the selectivity of the oligomerization method in accordance with the invention and to delay the catalyst deactivation. A limiting of the oligomer concentration can be achieved by reducing the duration in the reaction zone, i.e., an increase in the flow velocity. In that connection, it is advantageous to return a partial flow consisting of the hydrocarbon flow that contains no oligomers, exits from the last reaction zone and essentially consists of unreacted olefins and/or saturated hydrocarbons to the first reaction zone. The weight ratio between return flow and fresh supply of hydrocarbon is 0.5 to 10, preferably 1 to 7 and particularly preferred 1 to 4, in which case these values relate to the stationary state of the reaction system.

It was determined that the catalyst volume required to achieve high olefin reaction rates of 95% or higher may become very large in the case of a preferred limiting of the maximum oligomer percentage content in the reaction hydrocarbon mixture to values of less than 30% by weight, particularly at a low olefin concentration. It was also found that the total catalyst volume can be very much reduced when the oligomerization process is performed in a two-stage cascade, in which case a part of the hydrocarbon flow that does not contain any of the oligomers formed in the respective stage is returned upstream of the respective stage.

Accordingly and furthermore, the invention concerns a method for the oligomerization of $C_2$-$C_8$-olefins, in which

- a flow of an olefin-containing hydrocarbon mixture is as part of a first reaction phase guided across a heterogeneous catalyst that contains nickel,

- the formed oligomers are separated from the hydrocarbon flow after the first reaction stage and hydrocarbon flow I containing none of the formed oligomers is divided into partial flows Ia and Ib,

- partial flow Ia is returned to the first reaction stage and partial flow Ib is guided across a heterogeneous catalyst bed that contains nickel as part of a second reaction

phase,

- the formed oligomers are separated from the hydrocarbon flow after the second reaction phase and the hydrocarbon flow II that contains none of the formed oligomers is divided into two partial flows IIa and IIb,

- partial flow IIa is returned to the second reaction phase and the other partial flow IIb is removed from the process,

- and in which the ratios between Ia/Ib and IIa/IIB are selected such that the oligomer concentration in the reaction mixture does not exceed 30% by weight in any reaction stage.

The above representations, particularly with respect to the catalyst and hydrocarbon mixture used here, also apply to this aspect of the invention, unless the context indicates otherwise.

The first and/or second reaction phase preferably include several successive reaction zones that are operated adiabatically as described above.

The ratio between the percentage content of the total yield between the first reaction stage and second reaction stage preferably varies between 1.5:1 to 5:1 and particularly between 2:1 and 4.5:1.

The invention will be explained in more detail with the help of the figure and the following example.

Figure 1 is a schematic representation of a device that can be used to execute the method in accordance with the invention. The device includes the two reaction stages (100) or (200), each of which consists of the two reaction zones (110; 120) or (210; 220). The reaction mixture is cooled in the heat exchangers (102) or (202) between the two reaction zones. The hydrocarbon mixture is heated in the heat exchangers (102) or (202) to the respective inlet temperature. After exiting the first reaction stage, the reaction mixture is piped through the pipe (103) to the distillation column (104), where the formed oligomers are separated and removed through the pipe (105). The unreacted olefins and saturated hydrocarbons are taken from pipe (106) and are partially returned to the first stage and partially to the second reaction stage through the pipe (107). The ratio between the returned flow and the flow piped to the second stage is selected such that a given oligomer concentration is not exceeded at the outlet of the reactor (100). In the distillation column (204), the reaction mixture from the second stage is separated into formed oligomers and unreacted olefins or saturated hydrocarbons. The latter are partially returned to the second stage through the pipe (206) and are partially piped through the pipe (207) out of the process. The ratio between the returned flow and the piped-out flow is selected such that a given oligomer concentration is not exceeded at the outlet of the reactor (200).

Example: Mathematical simulation of an olefin oligomerization method.

The reaction of a hydrocarbon mixture to be used and of the following composition on a catalyst that was produced in accordance with DE-43 39 713 in the form of pellets of the size 5 mm x 5 mm (composition in % by weight of the active components: NiO 50% by weight, $TiO_2$ 12.5% by weight, $SiO_2$ 33.5% by weight, $Al_2O_3$ 4% by weight) was simulated with the help of the Aspen plus software (Release 9.3) produced by the firm Aspen Tech, Stanford. The calculations are based on a kinetic model of the reaction that was prepared by mathematically adjusting many experimental measuring results.

One calculated the catalyst volume that is required for a single-stage or two-stage operation with a different distribution of the total yield to the two stages (4:1 or 2:1) to achieve a total yield of 95% of octenes and dodecenes in relation to the butene content of the mixture used. The catalyst volume for a single-stage operation was arbitrarily set at 100%. The basis was formed by return flows that will lead to a maximum concentration of 20% by weight for the oligomers formed in the reaction mixture in the respective reaction stage. The results are summarized in the following table.

Composition of the hydrocarbon mixture used:

| | |
|---|---|
| i-butene | 0% by weight |
| i-butane | 4.87% by weight |
| 1-butene | 17.15% by weight |
| cis-2-butene | 16.14% by weight |
| trans-2-butene | 42.37% by weight |
| n-butane | 19.48% by weight |

Table:  Relative catalyst volumes required to achieve a yield of 95%

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| | |
|---|---|
| Single-stage operation | 100% |
| Two-stage operation 4:1 | 75% |
| 2-stage operation 2:1 | 55% |

1.  A method for the oligomerization of $C_2$-$C_8$-olefins, in which a flow of an olefin-containing hydrocarbon mixture is guided successively through "n" adiabatically operated reaction zones on a heterogeneous catalyst that contains nickel, where $n \geq 2$, in which case the hydrocarbon mixture experiences a temperature increase $\Delta T_{react.}$ in each reaction zone and the hydrocarbon mixture enters the first reaction zone at a temperature of $T_{enter}$ and is prior to entering the next reaction zone cooled to a temperature that is higher or lower than $T_{enter}$ by up to 20 °C, characterized by the fact that the respective catalyst volumes of the individual reaction zones are sized such that the $\Delta T_{react.}$ difference does not exceed 20 °C when comparing two reaction zones.

2.  A method in accordance with claim 1, in which the difference of $\Delta T_{react}$ does not exceed 10 °C.

3.  A method in accordance with claim 1 or 2, in which $T_{enter}$ shall be selected higher with an increasing catalyst service.

4.  A method in accordance with one of the previous claims, in which two reaction zones are used and the ratio between the catalyst volume at the first reaction zone and the catalyst volume at the second reaction zone varies between 30:70 and 45:55.

5.  A method in accordance with one of the previous claims, in which $T_{enter}$ varies between 20 and 120 °C.

6.  A method in accordance with one of the previous claims, in which the maximum oligomer concentration is limited to 30% by weight in relation to the reaction hydrocarbon mixture.

7.  A method in accordance with claim 6, in which a partial flow of the hydrocarbon flow, from which the oligomers were removed and that exits from the nth reaction zone, is returned to the first reaction zone.

8.  A method in accordance with one of the previous claims, in which the hydrocarbon flow is in the liquid phase.

9.  A method for the oligomerization of $C_2$-$C_8$-olefins in which

    -   a flow of an olefin-containing hydrocarbon mixture is as part of a first reaction phase guided across a heterogeneous catalyst that contains nickel,

    -   the formed oligomers are separated from the hydrocarbon flow after the first reaction stage and hydrocarbon flow I containing none of the formed oligomers is divided into partial flows Ia and Ib,

    -   partial flow Ia is returned to the first reaction stage and partial flow Ib is guided across a heterogeneous catalyst bed that contains nickel as part of a second reaction phase,

- the formed oligomers are separated from the hydrocarbon flow after the second reaction phase and the hydrocarbon flow II from which the formed oligomers were separated is divided into two partial flows IIa and IIb,

- partial flow IIa is returned to the second reaction phase and the other partial flow IIb is removed from the process,

- and in which the ratios between Ia/Ib and IIa/IIb are selected such that the oligomer concentration in the reaction mixture does not exceed 30% by weight in any reaction stage.

10. A method in accordance with claim 9, characterized by the fact that the ratio between the total yield percentage of the first reaction stage and the second reaction stage varies over a range of between 1.5:1 and 5:1.

Figure 1

/INTERNATIONAL SEARCH REPORT ALREADY IN ENGLISH/